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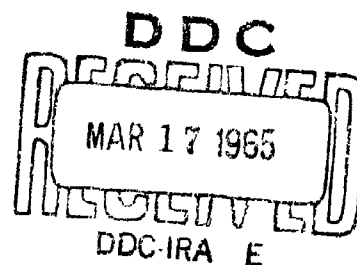
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✓ NITROGEN-15 TRACER STUDIES OF THE
NITROLYSIS OF HEXAMETHYLENETETRAMINE

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Introduction

The nitrolysis of hexamine to HMX/RDX has been studied in these laboratories (1) and using essentially the same conditions of the Holston Ordnance Works (HOW) process (2), which in turn is based on the Bachmann method (3), similar yields of products were obtained. By including a small quantity of paraformaldehyde $(\text{CH}_2\text{O})_x$ in the reaction mixture (hereafter called the PA process) the yield of mixed products was increased by approximately 10%. A study was carried out in which either hexamine or $(\text{CH}_2\text{O})_x$ was tagged with carbon-14 and the distribution of activity in the cyclic methylene nitramine products was traced during the course of nitrolysis (4). It was concluded that in the first reaction stage, methylene groups from hexamine and $(\text{CH}_2\text{O})_x$ form a common pool for the formation of DPT molecules. Similarly, in the second stage methylene groups from DPT and $(\text{CH}_2\text{O})_x$ also form a common pool for the formation of HMX and RDX molecules. Therefore, the relative ratio of HMX to RDX is not controlled by the selective cleavage of a large molecule but is more than likely influenced by the particular conditions controlling the recombination of a common methylene containing fragment. It was thus postulated that the $(\text{CH}_2\text{O})_x$ increases the concentration of methylene containing fragments which exist in precursors to HMX/RDX. The increase in yield of combined HMX/RDX products, resulting from the use of $(\text{CH}_2\text{O})_x$, can therefore be accounted for on this basis.

The methylene content is not the only criterion in controlling yield or composition of product. It is obvious that the processes involving amino groups and the formation of the nitramine structure are equally important for understanding the chemistry of hexamine nitrolysis. An indirect attempt was made to ascertain the extent to which the ammonium nitrate participates in the formation of HMX/RDX in the PA process (4). Carbon atom equilibration was found independent of the amino-nitrogen concentration. On the basis of this observation it was concluded that $(\text{CH}_2\text{O})_x$ does not react independently with ammonium nitrate to form HMX or RDX. In a more direct manner,

by using ammonium nitrate tagged with N-15 in the amino-nitrogen position, Bachmann (5) carried out some exploratory work to determine the role played by the ammonium radical in the formation of RDX (together with HMX as the minor constituent). The results obtained were complicated by the observed isotopic exchange of amino-nitrogens in hexamine and ammonium nitrate. In spite of the complications introduced by interchange, it was concluded that the formation of RDX involves more interaction with ammonium nitrate (37%) by exchange or incorporation or both, than does the formation of HMX (15%).

These results demonstrated the possibility of also obtaining some information directly on the participation of ammonium nitrate in the PA and HOW processes of HMX formation. Experiments were therefore conducted along lines similar to those described in Reference (4) with the exception that products were assayed mass spectrometrically for N¹⁵/N¹⁴ ratios.

Results and Discussion

Since the products DPT, HMX and RDX contain two types of nitrogen $\text{-CH}_2\text{-N-NO}_2$, the method for the conversion of amino-nitrogen to N₂ for mass spectrometric analysis was checked for specificity. Standard samples of HMX and RDX were prepared from $(\text{CH}_2\text{O})_x$ and ammonium nitrate of known N-15 atom percent as the sole source of amino-nitrogen. A sample of the N¹⁵H₄NO₃/HNO₃ used in this study, was included for analysis to check the possibility of exchange taking place between the nitrate-nitrogen and amino-nitrogen prior to the addition of reactants in the HOW and PA processes. The N-15 atom percent in all of the compounds analyzed mass spectrometrically was found to be within $\pm 0.2\%$ of the value for the N¹⁵H₄NO₃ reference standard. These results clearly establish the lack of nitro and/or nitrate-nitrogen participation in the generation of elemental amino-nitrogen, induced either during analysis or by exchange in a nitric acid medium. Therefore, it can be concluded that any interchange of nitrogen atoms that may be observed to take place during the nitrolysis of hexamine with NH₄NO₃/HNO₃ involves amino-nitrogens only.

Bachman (5) observed exchange to take place between hexamine and ammonium nitrate in acetic acid solution and assumed that exchange took place during nitrolysis. The process of exchange in inert media need not necessarily take place in reaction mixtures. Although hexamine and formaldehyde were found to exchange in an acidic aqueous medium (6), $(\text{CH}_2\text{O})_x$ does not exchange with hexamine under conditions of nitrolysis (4). Therefore, to determine whether the exchange reported by Bachman (5) does indeed complicate the study of the PA and HOW processes with N-15, exchange was studied under actual conditions of nitrolysis.

The atom percentages of N-15 found in the hexamine are listed in Table I. The average percent exchange, based on 2.4 atom % N-15 calculated for the complete equilibration of hexamine and ammonium nitrate amino-nitrogens, is seen to be independent of the amount of $(\text{CH}_2\text{O})_x$ included in the reaction mixture. The chief

significance of these results is that the rate of exchange of amino-nitrogens is faster than the rate of reaction during the nitrolysis of hexamine in the presence or absence of $(\text{CH}_2\text{O})_x$. It may be helpful at this point to emphasize the difference between "exchange" and "reaction" processes. Although exchange does proceed by means of reactions, the structural configuration of the interchanging species remain unaltered at the steady state of dynamic equilibrium. "Reaction" on the other hand proceeds in one direction only with the initial constituents transformed to different entities at a "static" state of equilibrium.

Table I
Amino-Nitrogen Exchange^(a) Between
Hexamine and NH_4NO_3 ^(b) In a Nitrolyzing Medium

	Expt. No.	Replicate No.	Atom % N-15 Found In Hexamine ^(c)	Average % Exchange ^(d)
Without $(\text{CH}_2\text{O})_x$	1	1	0.91	24
		2	0.84	
	2	1	0.87	
		2	0.73	
With $(\text{CH}_2\text{O})_x$	1	1	0.96	24
		2	0.92	
	2	1	0.73	
		2	0.72	

(a) All reactants added simultaneously and the mixture quenched with CCl_4 after 2 minutes.

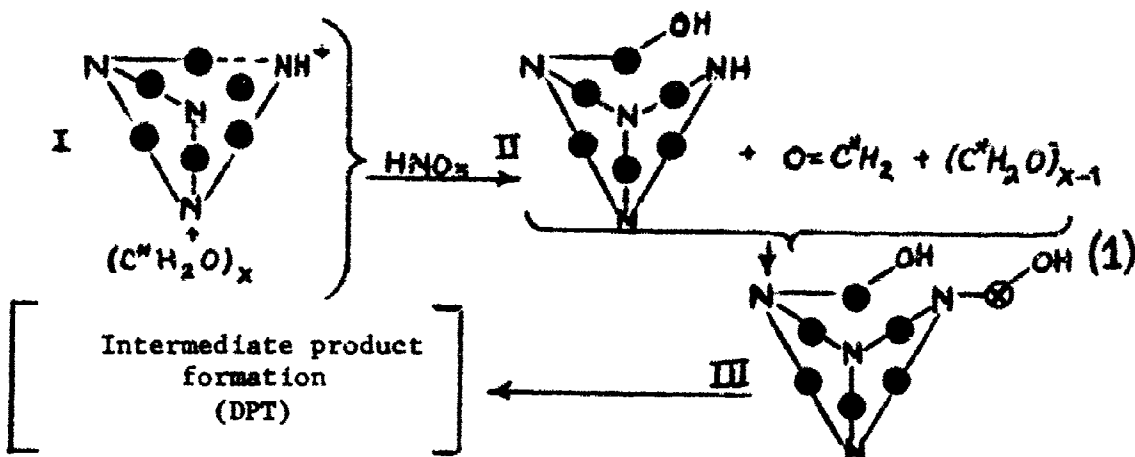
(b) Added as the nitric acid solution and containing 7.6 atom % N-15.

(c) Isolated as the mercuric chloride salt.

(d) Based on 2.4 atom % N-15 calculated for 100% exchange.

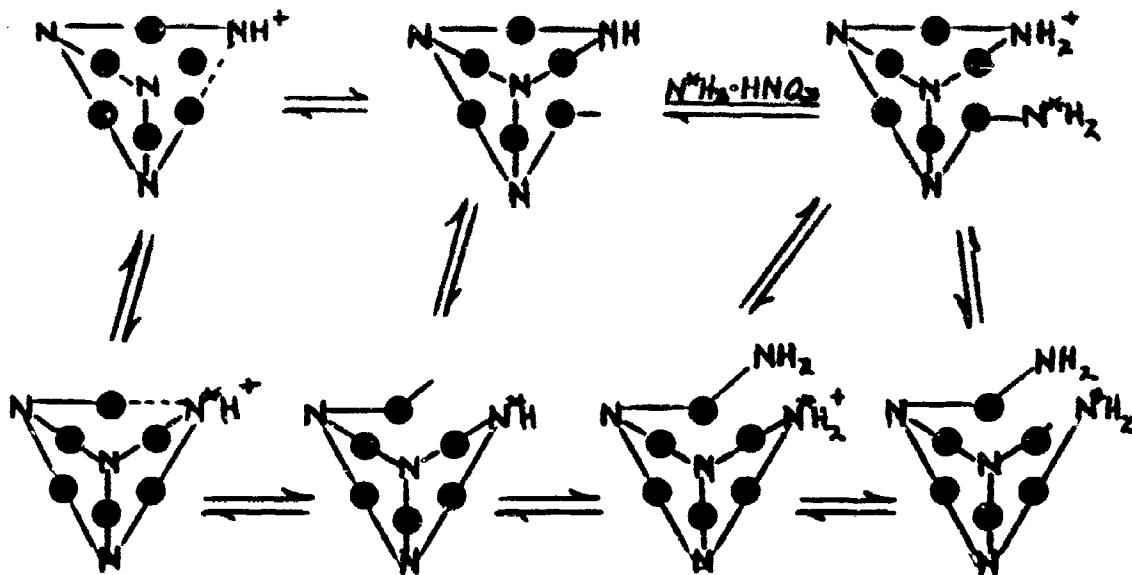
The question arises as to why the amino-nitrogens and not the methylene groups in the hexamine molecule exchange under conditions of nitrolysis. Exchange reactions are usually ionic and faster than metathesis reactions. Therefore, conditions conducive to exchange in competition with reactions would involve interchange between ionic species. Since $(\text{CH}_2\text{O})_x$ cannot be considered ionic in an acidic medium, even though hexamine is, the possibility of exchange is minimized and participation via reaction is favored (4). By way of inference only, the representation given below indicates the chemically equivalent nature of the methylene groups that can exist in a nitrolyzing medium. In an acidic medium hexamine exists as a protonated ion with a labile $-\text{CH}_2---\text{NH}^+$ bond. In an oxidizing medium this bond is subject to attack together with the bonds in the polymeric chain of $(\text{CH}_2\text{O})_x$ as shown in Diagram 1. In this mechanism, the implication is made that the reaction involving the fragmentation of $(\text{CH}_2\text{O})_x$ takes place irreversibly prior to equilibration and subsequent reaction leading to intermediate product formation. This is based on the experimental evidence given in Reference 4. Hexamine was isolated free of activity, indicating that III does not exist in

equilibrium with I but proceeds directly to form intermediate products. The configuration III may be considered the "common pool of methylene groups" to which reference was made in the work with carbon-14.



Where $\text{---}\bullet\text{---} \equiv \text{---CH}_2\text{---}$; $\text{C}^* \equiv \text{C}^{14}$ and $\text{---}\oplus\text{---} \equiv \text{---C}^{14}\text{H}_2\text{---}$

The path of amino-nitrogen exchange between hexamine and ammonium nitrate must undoubtedly involve both species in an ionic metastable state. The charged amino group of the metastable species, I, can then interchange with its equivalent nitric acid salt of ammonia as follows:



Where $\text{---}\bullet\text{---} \equiv \text{---CH}_2\text{---}$; $\text{N}^* \equiv \text{N-15 enriched}$; and $\text{N} \equiv \text{unenriched N-15 (i.e., in natural abundance)}$.

This implies that an exchange of amino-nitrogens takes place before nitrolysis and even before $\text{R-CH}_2\text{---}$ goes to $\text{R-CH}_2\text{---OH}$ or some equivalent irreversible substitution, in which case the rate of exchange is

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necessarily faster than the rate of reaction ($R =$ residual hexamine molecule).

According to the above suggested process of amino-nitrogen exchange, any DPT isolated from the addition of N-15 ammonium nitrate during the first stage of nitrolysis should contain N-15 enrichment corresponding to 100% exchange. This, of course, is based on the fact that all of the amino-nitrogens in hexamine are chemically equivalent, having a common $(CH_2)_3N$ configuration. The experimental atom-percent N-15 values found in the DPT are listed in Table II. As expected, these values are identical to the 2.4 atom % N-15 calculated for 100% exchange of hexamine and ammonium nitrate-amino nitrogens. Here again, exchange is shown to be independent of the $(CH_2O)_x$ concentration.

Table II

$NH_4NO_3^{(a)}$ Exchange In The Formation of DPT				Average % Exchange ^(b)
	Expt No.	Replicate No.	Atom % N-15 Found In DPT	
Without $(CH_2O)_x$	1	1	2.5	102
		2	2.5	
	2	1	2.4	
		2	2.4	
With $(CH_2O)_x$	1	1	2.4	102
		2	2.4	
	2	1	2.5	
		2	2.5	

(a) Added as the nitric acid solution and containing 7.6 atom % N-15.

(b) Based on 2.4 atom % N-15 calculated for 100% exchange of hexamine and ammonium nitrate-amino nitrogens.

The incompleteness of the exchange shown in Table I can, therefore, be attributed to the mode of addition and the time of contact of the reactants. Because complete equilibration of the four amino-nitrogens occurs prior to reaction, no conclusion can be drawn concerning the extent, if any, to which the ammonium nitrate directly participates in the formation of the DPT.

To investigate the step-wise role of ammonium nitrate in the HOW process the $N^{15}H_4NO_3/HNO_3$ was added during the second stage of nitrolysis and the HMX/RDX was analyzed for N-15 enrichment. Thus, the formation of HMX/RDX from DPT with any N-15 enrichment can be attributed solely to the participation of the ammonium nitrate added during the second stage of nitrolysis. Assuming that all of the amino-nitrogens, including the ones with nitro-substitutions, exchange during this second stage, the atom-percent N-15 calculated for HMX/RDX is 2.48%. The actual atom-percent N-15 found in HMX and RDX as listed in Table III are seen to be approximately half the calculated value, 2.48%.

The amino-nitrogens in DPT contain two types of substitutions, $(CH_2)_3N$ and $(CH_2)_2N-NO_2$ where only the former is, of course, common to

hexamine and shown to exchange completely. The observed incomplete exchange during the second stage of nitrolysis may, therefore, be attributed to the nitrosubstituted amino-nitrogen which fails to exchange.

Table III

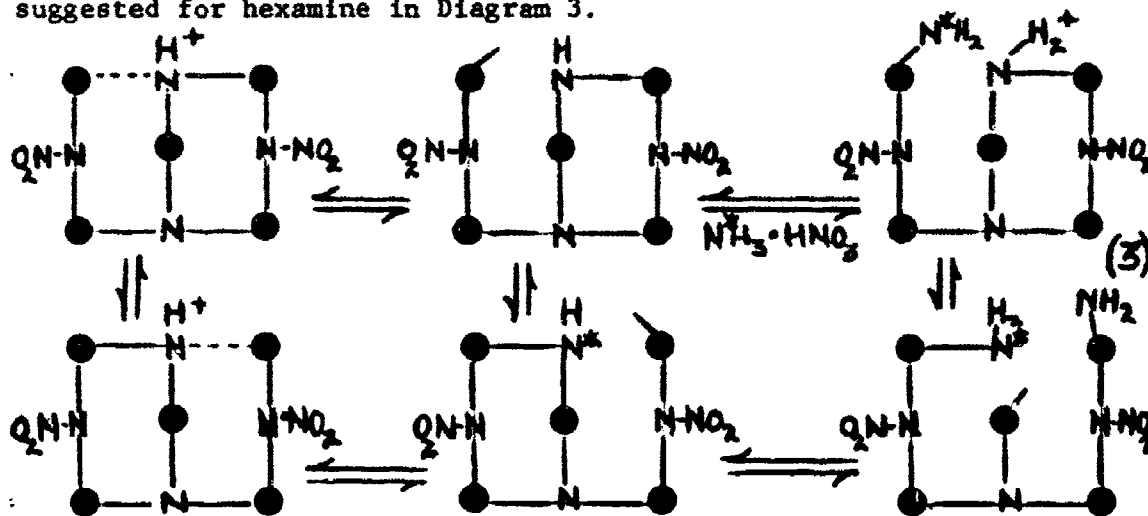
$\text{NH}_4\text{NO}_3^{(a)}$ Participation In The Formation of HMX/RDX
In The Absence of $(\text{CH}_2\text{O})_x$

Expt No.	Replicate No.	Atom % N-15 Found		Avg % NH_4NO_3 Participation	
		HMX	RDX	HMX(b)	RDX(b)
1	1	1.3	1.5	0	6
	2	1.5	1.5		
2	1	1.2	1.2		
	2	1.2	1.4		

(a) 7.6 atom % $\text{N}^{15}\text{H}_4\text{NO}_3$ added as the nitric acid solution during the second stage of nitrolysis.

(b) HMX and RDX as derived from NH_4NO_3 amino-nitrogens solely due to reaction.

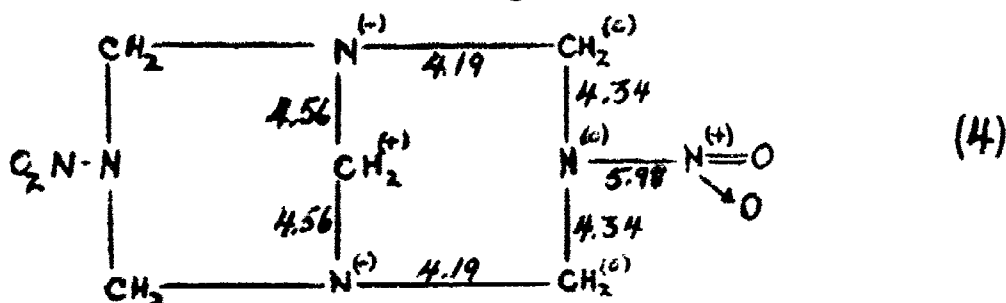
The equilibration of amino-nitrogens due to exchange being limited to the $(CH_2)_3N$ substitutions in DPT, would follow the course suggested for hexamine in Diagram 3.



Here again exchange proceeds before the methylene radical undergoes reaction to form stable products. Thus the DPT molecule contains two of its four amino-nitrogens with N-15 enrichment prior to irreversible transformation. In the case of $(\text{CH}_2)_2\text{N}-\text{NO}_2$ the amino-nitrogen does not equilibrate with the ammonium adduct based on the assumption that the N- NO_2 bond is stable under the prevailing conditions of nitrolysis.

Calculations of bond force constants based on stretching vibrations lend substantiative evidence to the above suggested mode of exchange during the second stage of nitrolysis. The method of calculation according to Gordy (7) is considered a very good approximation of relative bond strengths of the type of bonds found in DPT. The

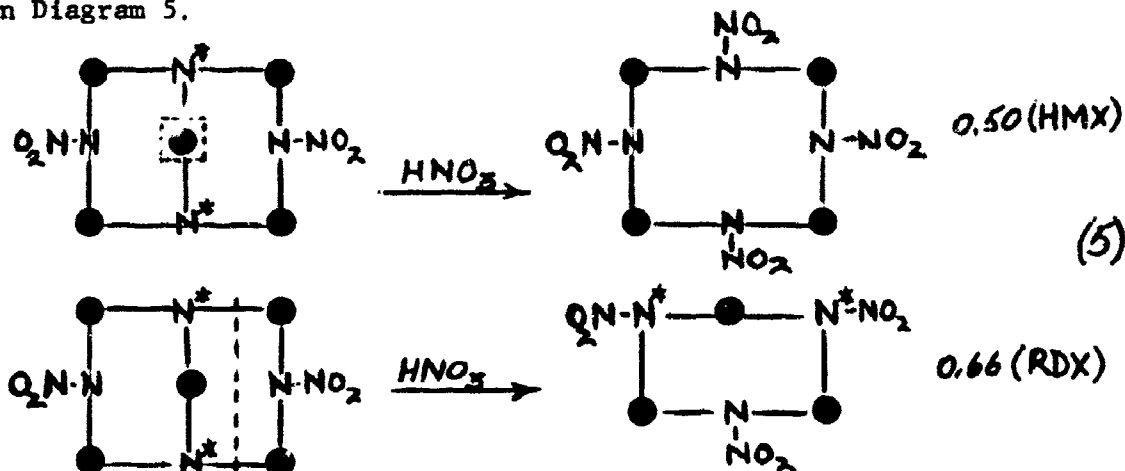
values of the bond stretching force constants ($\times 10^5$ dynes/cm) obtained for the DPT molecule are shown in Diagram 4.



The symbol in parentheses is the induced charge or relative electronegativity assigned to the atom. It can be readily seen that the N-NO₂ bond is indeed the strongest type bond in DPT. Therefore, it is reasonable to assume that this bond is stable in a nitrolyzing medium and being strongly covalent does not undergo exchange.

NH₄NO₃ Participation in the HOW Process

When N¹⁵H₄NO₃ is added during the second stage the N-15 enrichment is, therefore, expected to be present only in the trimethylene substituted amino-nitrogen prior to reaction. Because of this selective exchange it was possible to determine the role of ammonium nitrate during the second stage as well as the mode of HMX/RDX formation from DPT. If selective cleavage of DPT were to take place in the formation of products, 0.50 and 0.66 of the amino-nitrogen in HMX and RDX, respectively, would contain N-15 enrichment, as indicated in Diagram 5.

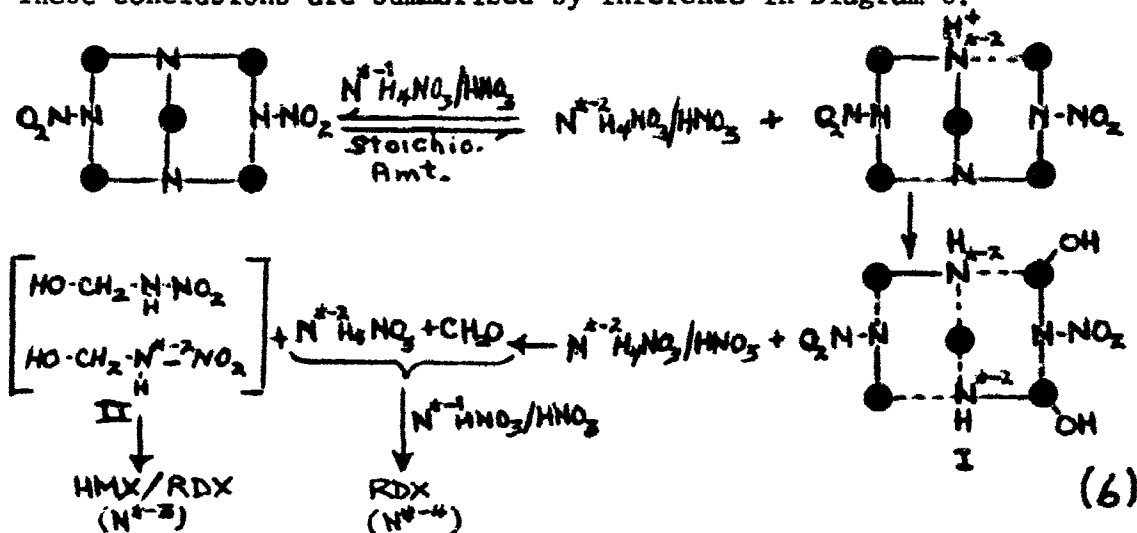


The ratio of atom % N-15 in HMX/RDX should be 0.50/0.66 or 0.75 if the above mechanism were indeed the mode of HMX and RDX formation. As can be seen in Table III the average ratio of atom % N-15 in HMX/RDX formed in the absence of (CH₂O)_x is 0.93 or essentially unity. To check these results, in one series of experiments N¹⁵H₄NO₃ was added during the first stage. In another series, N¹⁵N₄NO₃ was added during both the first and the second stages. In each case, only the HMX and RDX were analyzed for atom % N-15 content. The results are listed in

Table IV and show an over-all average atom % N-15 of 0.97 in HMX/RDX for each respective series.

The following conclusions which can be drawn from this observed N-15 ratio give a direct insight into modes of reaction that may take place during the second stage of nitrolysis in the absence of $(\text{CH}_2\text{O})_x$:

- DPT does not cleave selectively to form HMX and RDX.
 - HMX and RDX are derived essentially from hexamine nitrogens.
 - HMX and RDX are derived from equilibrated $-\text{CH}_2-\text{N}-\text{NO}_2$ fragments, half of which are formed during the first stage and the other half during the second stage.
 - A small fraction of approximately 5% of RDX is derived from ammonium nitrate.
 - The rate of formation of HMX is greater than that of RDX.
- These conclusions are summarized by inference in Diagram 6.



Where the atom % N-15 of $\text{N}^{*-1} > \text{N}^{*-4} > \text{N}^{*-2} > \text{N}^{*-3}$ and N = natural abundance. The ratio of the $\text{HO}-\text{CH}_2-\text{NH}-\text{NO}_2/\text{HO}-\text{CH}_2-\text{NH}^{*-2}-\text{NO}_2$ mixture in II is essentially equal to one, since the major product is DPT. Therefore, there is an equal distribution of N-15 and N-14 atoms in HMX and RDX derived therefrom. However, after the formation of II the $\text{N}^{*-1}\text{H}_4\text{NO}_3$ in the ammonium nitrate-nitric acid mixture is in excess of the hexamine nitrogens. This N-15 ammonium nitrate, which cannot exchange with the now completely nitro-substituted hexamine nitrogens, exchanges instead with the ammonium nitrate in situ. Any product formed from the ammonium nitrate amino-nitrogen would obviously have a higher atom % N-15 than a product formed from hexamine-nitrogen. The extent of this increase is proportional to the formation of product from ammonium nitrate. With these factors taken into consideration and correcting for the incomplete conversion of $-\text{CH}_2-\text{N}-\text{NO}_2$ to products, calculations of the atom % N-15 due to exchange alone and, therefore, implying the involvement of hexamine nitrogens only are in excellent agreement with the values shown by analysis for HMX

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in Tables III and IV. Therefore, the extent of ammonium nitrate participation in HMX formation is zero as shown in the last column of Tables III and IV. The atom % N-15 found in RDX is on the average, 4% greater than the calculated value for exchange and is attributed to ammonium nitrate participation. Calculations of the ammonium nitrate participation according to the reaction path as outlined in Diagram 6 show values corresponding to this observed atom % N-15 difference.

The condensation of **I** to products may be considered as a function of competing rates controlled by a concentration effect. It is conceivable that the rate of HO-CH₂-NH-NO₂ cyclization is faster for HMX than for RDX formation. This is based on the fact that the C-N bond angles in HMX are less strained than those in RDX. As the cyclization of the common precursor is brought to completion, the nitric acid content in the reaction mixture is reduced to negligible proportions. The ammonium nitrate and acetic anhydride concentrations are concurrently increased, approaching conditions similar to those in the Ross process (8). In that process, RDX is formed with HMX as a contaminant predominantly from the condensation of (CH₂O)_x with ammonium nitrate by the action of acetic anhydride. Therefore, because of these conditions prevailing during the latter stages in the HOW process, the residual formation of RDX is favored from ammonium nitrate and the available methylene-containing species equivalent to formaldehyde.

Table IV

Check Determination of NH₄NO₃ Participation in The
Formation of HMX/RDX In The Absence of (CH₂O)_x

N ¹⁵ H ₄ NO ₃ (a) Addition	Expt. No.	Repli- cate No.	Atom % N-15 Found		Avg % NH ₄ NO ₃ Participation	
			HMX	RDX	HMX (b)	RDX (b)
1st Stage	1	1	1.8	1.9	0	0
		2	1.8	1.7		
	2	1	1.7	-	0	0
		2	1.7	-		
1st & 2d Stages	3	1	2.4	2.5	0	6
		2	2.5	2.7		

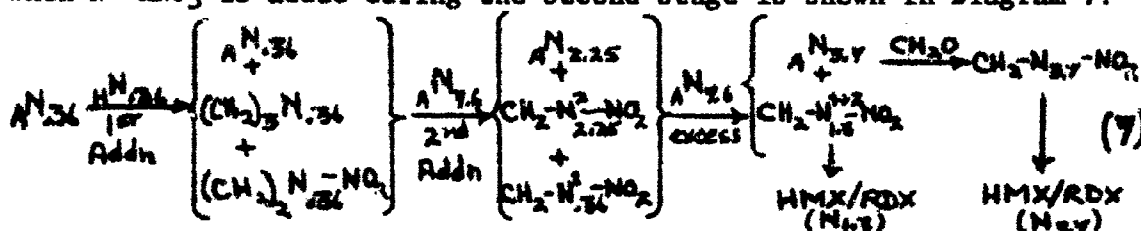
(a) Added as the nitric acid solution and containing 6.42 atom % N-15.

(b) HMX/RDX as derived from NH₄NO₃ amino-nitrogens solely due to reaction.

NH₄NO₃ Participation in the PA Process

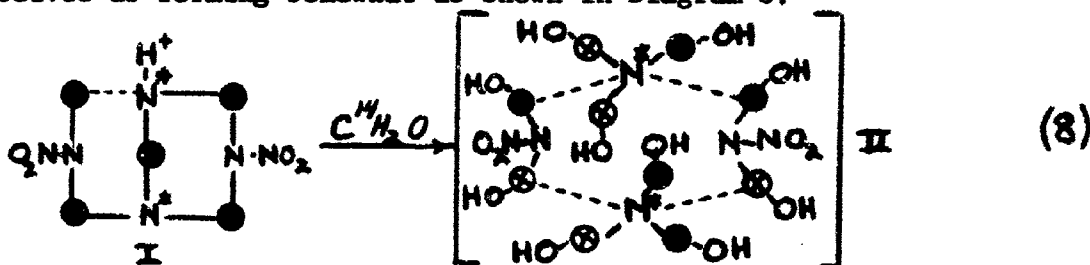
In tracing the role of ammonium nitrate in the presence of (CH₂O)_x, N¹⁵H₄NO₃ was added during the second stage of nitrolysis. Check determinations were made by adding N¹⁵H₄NO₃ during the first stage and in another set during both the first and the second stages. The N-15 enrichments found in the HMX and RDX are listed in Table V. These values imply that the reaction sequences, although complicated by the inclusion of (CH₂O)_x, are nevertheless comparable to the ones outlined above for the HOW process. In major part, this mechanism

is used for the interpretation of the N-15 values obtained in the PA process. The distribution of N-15 enrichment in the reaction sequences when $N^{15}HNO_3$ is added during the second stage is shown in Diagram 7.



Where A^N = ammonium nitrate amino-nitrogen, H^N = hexamine amino-nitrogen, N^1 = nitro-substitution formed during 1st addition, N^2 = nitro-substitution formed during 2d addition. According to this mechanism the calculated over-all average percent ammonium nitrate participation shown in Table V is 8% for HMX and 40% for RDX (see experimental procedure for sample calculation).

The suggested mechanism must, of course, be compatible with the results obtained from the study with carbon-14 (4). In that study, the methylene groups from hexamine and $(CH_2O)_x$ were shown to equilibrate during the second as well as during the first stage of reaction. For such an equilibration to take place a metastable intermediate of the form $O_2N-N-(CH_2OH)_2$ must exist which then proceeds to form the common monomer precursor to HMX and RDX, $HO-CH_2-NH-NO_2$ as shown for I in Diagram 6. The common pool of methylene groups may be conceived as forming somewhat as shown in Diagram 8.



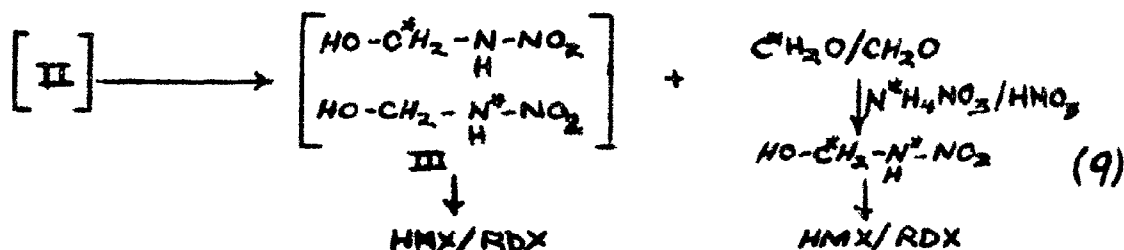
Where N^* = N-15 enriched, $-C^{14}H_2-$ = $-C^{14}H_2-$, $-CH_2-$ = $-CH_2-$

The DPT with N-15, I, is included to demonstrate the concurrent behavior of amino-nitrogens and methylene groups and may be looked upon as a continuation of the preceding step involving selective amino-nitrogen exchange indicated in Diagram 6. It must be emphasized again the the equilibration of methylene groups following amino-nitrogen exchange is due to reaction and not exchange; and that these processes are, therefore, independent of each other.

It is not to be construed that II in Diagram 8 actually exists as such, but what is solely intended is to illustrate the probable existence of an intermediate specie which can explain the experimentally observed chemical equivalence of methylene groups and amino-nitrogens. The pool of amino-nitrogens and methylene groups as is intimated by II, is then thought of as forming a common monomer precursor, III (Diagram 9), analogously to the path indicated by II

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in the series of reactions shown in Diagram 6.



Here again, the participation of ammonium nitrate must take place, in this case after the release of the equilibrated hexamine and $(\text{CH}_2\text{O})_x$ methylene groups resulting from the cyclization of III to HMX and RDX. This conclusion is not only supported by the excellent agreement between the observed atom % N-15 and the calculated values based on the proposed mechanism, but also by the results obtained in the Carbon-14 tracer study. When C-14- $(\text{CH}_2\text{O})_x$ was added during the second stage an equal distribution of activity was observed in HMX and RDX, signifying methylene carbon equilibration. If any direct condensation of ammonium nitrate with $(\text{C}^*\text{H}_2\text{O})_x$ had occurred prior to equilibration, the carbon-14 content of the RDX would have been significantly greater than that of the HMX, since 40% of RDX and only 8% of HMX is derived from ammonium nitrate.

Table V

NH_4NO_3 Participation in The Formation
of HMX/RDX In The Presence of $(\text{CH}_2\text{O})_x$

$\text{N}^{15}\text{H}_4\text{NO}_3$ (a) Addition	Expt Replicate No.		Atom % N-15 Found		Avg % NH_4NO_3 Participation HMX(b) RDX(b)	
			HMX	RDX		
Second Stage	1	1	1.3	2.6	4	50
		2	1.6	2.3		
	2	1	1.4	2.4		
		2	1.2	2.6		
First Stage	3	1	1.7	1.6	10	40
		2	1.8	1.5		
	4	1	1.7	1.6		
		2	1.8	-		
1st and 2d Stages	5	1	2.7	3.1	9	37
		2	2.6	3.1		

(a) Added as the nitric acid solution and containing 6.42 atom % N-15 in Expts 1, 2 and 5; and 7.6 Atom % N-15 in Expts 3 and 4.

(b) HMX/RDX as derived from NH_4NO_3 amino-nitrogens solely due to reaction.

The final step in the PA process involving the condensation of methylene and ammonium fragments is shown by calculations, based on the experimental data to include the formation of HMX together with RDX, whereas in the HOW process only RDX was shown to form (see last column, Table V). The formation of approximately 8% HMX as well as

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the increased production of RDX from ammonium nitrate (5% in the HOW process as compared to 40% in the PA method) may be explained on the basis of the relatively high concentration of methylene fragments released from II in Diagram 9. Only one equivalent endo-methylene group is released in the HOW process while all of the methylene groups equivalent to those added in the form of $(CH_2O)_x$ and, in addition, the equivalent endomethyl group are released in the PA process. As the concentration of equilibrated methylene groups increases, their condensation with ammonium nitrate is driven to the right. The increased HMX yield as well as the increased over-all HMX/RDX yield of the PA process may be attributed in part to the final step of this postulated mechanism.

The relative rates of product formation mentioned above for the HOW process evidently prevail also in the PA process. The atom % N-15 in HMX is significantly less than that of RDX, indicating preferential HMX formation from hexamine nitrogens as compared to the more pronounced formation of RDX from ammonium nitrate. Correspondingly, the ratio of atom % N-15 in HMX/RDX is decreased from 0.96 in the HOW process to 0.56 in the PA process. Both values deviate appreciably from the 0.75 figure associated with the selective cleavage of the DPT molecule to discount the possibility of such a mechanism taking place in either process for HMX/RDX production.

Conclusions

The conclusions drawn from the data obtained in the earlier work with carbon-14 are substantiated by these tracer studies with nitrogen-15. In addition, a more complete understanding of the chemistry of amino groups and the processes involved in the formation of the nitramino structure has been obtained through the use of nitrogen-15.

With Carbon-14 indirect evidence had indicated that ammonium nitrate does not condense directly with $(CH_2O)_x$ to yield HMX and RDX. With nitrogen-15 this was shown directly to be the case.

The equilibration of methylene groups was found to be independent of ammonium nitrate concentration; and with nitrogen-15 tracing the equilibration of amino-nitrogens was shown to be independent of the $(CH_2O)_x$ concentration. The two processes are mutually independent of each other because their respective modes of equilibration are different. The equilibration of amino-nitrogens being ionic in character takes place by means of exchange and, therefore, precedes the equilibration of methylene groups, which is attributed solely to a reaction process.

It was concluded in the previous study with carbon-14 that hexamine and DPT degrade non-selectively to low molecular weight species which then recombine to form products. The existence of a selective cleavage mechanism has been discounted by data obtained with nitrogen-15 and with carbon-14. The complementary nature of the data obtained from the two studies makes possible the narrowing down of the common fragmentary precursor to HMX and RDX as being of the type, $HOCH_2NHNO_2$.

In the earlier work it was postulated that $(CH_2O)_x$ increases the concentration of methylene groups which exist in precursors to HMX

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and RDX. It was suggested that the increase in yield of combined HMX and RDX products results from inclusion of $(\text{CH}_2\text{O})_x$ could be accounted for on this basis. With nitrogen-15 it became possible to indicate how this actually can take place, viz., by the condensation of the increased concentration of equilibrated methylene fragments with the ammonium radical. The extent of this participation with ammonium nitrate is approximately 7% for the formation of HMX and 40% for RDX, which is indeed equivalent to the 10% over-all increase in HMX/RDX yields observed when $(\text{CH}_2\text{O})_x$ is included in the reaction mixture.

The evidence given for the existence of a common precursor to HMX/RDX of the type $\text{HOCH}_2\text{NHNO}_2$ justifies any effort to prepare HMX from monomethylene containing compounds. A more direct approach to the formation of HMX free of RDX contamination in a simple reaction medium would greatly reduce the current cost of production.

Experimental Procedure

The nitrolyses reactions and the isolation and purification of products (DPT, HMX and RDX) were carried out as described in References (4) and (6), with the exception of using $\text{N}^{15}\text{H}_4\text{NO}_3$ in place of the normal NH_4NO_3 wherever indicated in this report.

Hexamine Exchange Study

The exchange between hexamine and $\text{N}^{15}\text{H}_4\text{NO}_3$, in the absence as well as in the presence of $(\text{CH}_2\text{O})_x$ was studied under actual conditions of nitrolysis in the manner described in Reference (4). During the two-minute period of intermixing of reactants the temperature was permitted to rise to 44°C .

Preparation of HMX and RDX Standards for N-15 Mass Spectrometric Analyses

To a 150 ml three-neck, round-bottom flask are added 11.43 g of ammonium nitrate (of known atom % N-15) and 6.43 g of $(\text{CH}_2\text{O})_x$ dissolved in 25 ml of glacial acetic acid. The mixture is heated on a water bath to effect dissolution. With the solution at 40°C , 50.4 ml of acetic anhydride are added during a 30-minute period. Following this addition, the mixture is aged at 45°C for one hour; the temperature is then raised to 75°C for an additional 30-minute aging. Then the mixture is refluxed with 17 ml of water for 30 minutes. Finally 150 g of ice are added and the HMX and RDX separated in the usual manner.

Mass Spectrometric Analysis of Amino-Nitrogen N-15 Enrichment

All samples were analyzed by the Isomet Corporation, Palisades Park, New Jersey, under service contract. The specificity of their method for amino-nitrogen was checked by the preparation of HMX and RDX standards of known amino-nitrogen N-15 enrichments.

Sample calculation of atom % N-15 in HMX and RDX when $\text{N}^{15}\text{H}_4\text{NO}_3$ is added during the Second Stage

The quantities of N-15 and N-14 in hexamine and ammonium nitrate due to natural occurrence, viz., 0.36%, at end of First Stage are:

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$H^{N-15} = 0.00726$ g, $A^{N-15} = 0.00277$ g, $H^{N-14} = 2.018$ g, $A^{N-14} = 0.769$ g.
The ammonium nitrate added during the Second Stage, having 7.6 atom % N-15 contains: $1.154 \times .076 = 0.0877$ g N-15. Correcting for the amount of ammonium nitrate equivalent to the trimethylene substituted amino-nitrogen in DPT (.634) and for the incomplete conversion to final nitramine products (.85); i.e., $0.85 \times 0.634 = 0.539$.

The atom % N-15 at the end of the second addition is given by:

$$0.36\% + \left[\frac{.5(.00726) + .00277 + .539(.0877)}{.5(2.018) + .769 + .539(1.154)} \right] \times 100 = 0.36\% + 2.25\% =$$

$$2.61\% \text{ then } \frac{2.61}{2} = 1.3 \text{ atom \% N-15 in HMX/RDX}$$

$$\text{i.e., } \left[.5(\text{CH}_2-\text{N}-\text{NO}_2) = 0.18\% \right] + \left[.5(-\text{CH}_2-\text{N}^+-\text{NO}_2) = 1.1\% \right] = 1.3\%$$

1st Stage Formation

2d Stage Formation

After the addition of the stoichiometric quantity, the ammonium nitrate and the equivalent hexamine nitrogen contain 2.25 atom % N-15 and the excess ammonium nitrate contains the initial 7.6 atom % N-15. The interchange of these two ammonium nitrates yields an equilibrated specie with an atom % N-15 proportional to their respective mole fractions, i.e.

$$2.25 \times \left[\frac{.055 + .539(.082)}{.055 + .082} \right] + 7.60 \times \left[\frac{.461(.082)}{.055 + .082} \right] = 3.7\%$$

Therefore any product formed from ammonium nitrate contains 3.7 atom % N-15 in combination with product formed from hexamine with 1.3 atom % N-15. The relative amounts are obviously governed by the atom % N-15 found in the particular product.

For the RDX formed in the absence of $(\text{CH}_2\text{O})_x$, the percentages of RDX derived from the respective amino-nitrogens are given by: $1.3x + 3.7(1-x) = 1.5$; $x = 0.92$; i.e., 8% RDX derived from NH_4NO_3 amino-nitrogen, 92% RDX derived from hexamine amino nitrogen.

The HMX formed in the absence of $(\text{CH}_2\text{O})_x$ is solely derived from hexamine nitrogen since the atom % N-15 found in HMX is equal to the calculated value, 1.3%.

The RDX's formed in the presence of $(\text{CH}_2\text{O})_x$ are: $1.3x + 3.7(1-x) = 2.5$; $x = 0.50$; i.e. 50% RDX derived from NH_4NO_3 amino-nitrogen, 50% RDX derived from hexamine amino-nitrogen.

The HMX derived from NH_4NO_3 in the presence of $(\text{CH}_2\text{O})_x$ is given by: $1.3x + 3.7(1-x) = 1.4$; $x = 0.96$; i.e., 96% HMX derived from hexamine amino-nitrogen, 4% HMX derived from NH_4NO_3 amino-nitrogen.

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